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The extent of protonation of organic bases in clay-water systems depends upon the adsorptive properties of the organo-clay species involved, and upon the structure and degree of hydration of the clay system. Organic molecules that can disperse cationic charge over two or more condensed aromatic rings give rise to greater surface-induced protonation than do single-ring organic molecules with similar solution pK_a. Protonation in clay suspensions is frequently far in excess of that predicted on the basis of electrolytic suspension pH and solution pK_a of the organic base. For a given organic base, protonation in a clay film exceeds that in the suspended clay system. Protonation in an organo-clay film increases as the film moisture content decreases. The extent of protonation in organo-clay systems varies with cationic species, cationic saturation, and clay type.

The environmental impact that pesticides have can be greatly modified by this clay-water system.

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PROTONATION OF ORGANIC BASES IN CLAY–WATER SYSTEMS

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Abstract—The extent of protonation of organic bases in clay–water systems depends upon the adsorptive properties of the organo-clay species involved, and upon the structure and degree of hydration of the clay system. Organic molecules that can disperse cationic charge over two or more condensed aromatic rings give rise to greater surface-induced protonation than do single-ring organic molecules with similar solution pK_a. Protonation in clay suspensions is frequently far in excess of that predicted on the basis of electrolytic suspension pH and solution pK_a of the organic base. For a given organic base, protonation in a clay film exceeds that in the suspended clay system. Protonation in an organo–clay film increases as the film moisture content decreases. The extent of protonation in organo–clay systems varies with cationic species, cationic saturation, and clay type.

INTRODUCTION

Models for predicting pesticide behavior in the environment are currently being developed at the Athens Environmental Research Laboratory, with emphasis on agricultural runoff. Since the acidity of natural clay or soil surfaces determines to a large extent the chemical and physical behavior of many surface-absorbed molecules, surface acidity studies are important in elucidating the behavior of pesticide–soil–water systems (Armstrong and Chesters, 1968; Bailey *et al.*, 1968; Harter and Ahlrichs, 1969; Bailey and White, 1970; Mortland, 1970; Weed and Weber, 1974). Soil surfaces can serve as proton sources or sinks in pesticide–soil interactions. The gain or loss of one or more protons by a pesticide can alter its movement characteristics by changing the pesticide–soil particle interactions or by altering the solubility of the pesticide species. In addition, chemical attenuation of a pesticide can be altered significantly.

Protonic sources in soils are extremely varied and complex; protons may be available from organic acidic functional groups (*e.g.* carboxylic or phenolic) in a soil constituent or may be present as exchangeable cations on inorganic constituents. In addition, protons in colloidal clay systems may result from hydrolysis of the structural constituents or hydrolyis of inorganic cations (e.g. Fe^{3+}, Al^{3+}, Mg^{2+}) adsorbed on the clay surface (Mortland and Raman, 1968).

Clay mineral surface acidity has been the subject of intensive research for several decades. This acidity has been studied with respect to the chemistry of the clay structure and of specific adsorbed species (Russell *et al.*, 1968). Much effort has been expended in describing the nature and properties of the acidic sources. For our purpose, we consider the acidic sources in wetted clay systems to be those that are Brönsted or protonic in nature. Protons are either transferred directly to an organic base from a covalently bound source, equation (1), or are transferred via the adsorbed water network as hydrated protons, equation (2);

$$(\text{Clay–H}) + \text{B} \leftrightarrows \text{Clay}^-\text{–(HB)}^+ \quad (1)$$

$$(\text{Clay–H}) + \text{H}_2\text{O} \leftrightarrows \text{Clay}^-\text{–H}_3\text{O}^+ \quad (2a)$$

$$\text{Clay}^-\text{–H}_3\text{O}^+ + \text{B} \leftrightarrows \text{Clay}^-\text{–(BH)}^+ + \text{H}_2\text{O} \quad (2b)$$

where B is an organic base.

Because of the wide variety of acidic surface components in natural systems, it is more useful to study the general effects of acidic behavior rather than to study each structural component individually. Therefore we used acidity indicators to monitor the protonating ability of natural surfaces under various conditions. For indicators organic bases were selected that would contain the basic functional groups common to pesticides, and also respond to the expected range of acidity for the clay systems of interest (Table 1). We used u.v.-*vis* absorption spectroscopy to monitor the indicators, as described previously (Bailey and Karickoff, 1973), because it offers several advantages over other monitoring methods (Benesi, 1956; Harter and Ahlrichs, 1967; Tullock, 1970; Conley and Althoff, 1971; Frendel, 1974). It can measure protonation *in situ* under wet or dry conditions (*i.e.* suspension, slurry, or dry film) and it is very sensitive. Low levels of indicator loading [$<0.1\%$ cation exchange capacity (CEC) for some indicator–clay systems] can be quantitatively and reproducibly monitored.

MATERIALS AND METHODS

Absorbent material preparation

Clay minerals from Wards Scientific Establishment* (Table 1) were fractionated by sedimentation; particles <2 μm in equivalent spherical diameter were isolated and washed twice with distilled water to remove water soluble materials. To remove insoluble carbonates, the clay suspensions (0.1–1% by

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Table 1. Organic bases, adsorbent materials and humidity control salts

Organic base	pK_a^*
3-aminopyridine	6.0
5-aminoquinoline	5.4
2-amino-5-chloropyridine	4.8
atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine)	1.7
phenazine	1.2
4-nitroaniline	1.0

Adsorbent materials	
Montmorillonite no. 21	Kaolinite no. 4
Montmorillonite no. 24	White Store soil clay†
Montmorillonite no. 25	Iredell soil clay†
Hectorite No. 34	Berks soil clay†

Saturated salt solutions for r.h. control	Relative humidity at 25°C‡
NaOH	7.0
LiCl	11.3
$MgCl_2$	32.7
NaCl	75.1
KCl	84.2
K_2SO_4	97.0

* pK_a taken from Perrin (1965) with the exception of atrazine which was taken from Bailey and White (1965).
† B horizon.
‡ Young (1967).

weight) were percolated through an H^+-saturated cationic exchange column, degassed by stirring under vacuum, and passed through an OH^--saturated anionic exchange column. The suspension was then passed through a Na^+-column, degassed again, and stored in the Na^+ form for brief periods (<1 week) prior to use. The clay was not permitted to remain in the acid form for more than 10 min to minimize chemical aging, which is accelerated in the H^+-clay form. Fresh samples were prepared just prior to indicator treatment by percolating the Na^+-suspension through cationic exchange columns saturated with the desired cation. Rexyn AG-50 cation resin and Rexyn 201 anion resin were used throughout. Soil clays were particle-size fractionated as described above, but were neither decarbonated nor homoionically saturated prior to use.

Indicators

Stock solutions (approximately 10 ppm) of the indicators listed in Table 1 were prepared using reagent grade organics and degassed water. Spectroscopic absorptivities of the neutral and protonated forms of the indicators were determined both in water and in hectorite suspensions containing approximately 5 mg/l hectorite and 0.1 to 5 mg/l indicator. Dilute NaOH and HCl were used as needed to achieve the desired indicator forms.

Indicator–clay mixing

Indicator–clay suspensions were prepared by mixing (on a dropwise basis) aliquots of bulk clay and indicator solutions. Indicator–clay films were prepared by pipetting 1 ml aliquots of the indicator–clay suspensions onto fused silica discs (22 mm dia.) and drying in desiccators over silica gel or magnesium perchlorate. Spectroscopic blanks were prepared for all samples by substituting water for indicator in the sample preparation procedures. Care was taken to maintain degassed conditions throughout preparation and analytical procedures to avoid CO_2 effects on acidic behavior.

Spectroscopic analysis

All spectra were run on a Perkin-Elmer 356 spectrophotometer using an R-189 photomultiplier tube. Suspensions were run in sealed fused silica cells (1 cm path length) placed approximately 5 mm from the phototube. Indicator–clay and blank films were mounted in a cylindrical cell with the samples facing the cell interior (Fig. 1). The cell was partially filled (below the sample level) with the saturated salt solution required to achieve the desired humidity control (Table 1). The cell was placed in the instrument with the films approximately 3 mm from the phototube. Films taken from the drying desicators were allowed to equilibrate in the cell for approx. 30 min. Equilibration was judged to be complete when a stable spectroscopic response was obtained. The proximity of the samples to the phototube substantially reduces light scattering problems which have hampered u.v. studies of turbid media in the past; the high sensitivity characteristic of u.v. absorption can now be realized in clay media. Although all data reported herein were collected at room temperature, the experimental setup was designed so that temperature could be varied and controlled.

RESULTS

Studies of the adsorbate and adsorbent properties that affect protonation were primarily restricted to clay systems; protonation was monitored in selected soil–clay and soil systems but no extensive study in these systems was conducted. The protonation of adsorbates by clay mineral adsorbents was found to be dependent upon many properties of the indicator, the clay, and the system.

Indicator properties

The relative basicities of organic molecules as measured in aqueous solution (reflected by pK_a) differed considerably from their relative basicities as measured when either the neutral or protonated species was adsorbed. The adsorptive properties of the conjugate indicator species (B and BH^+ in equations 1 and 2) affected quite markedly the degree of protonation effected by a given surface (Table 2). Not

Table 2. Protonation* enhancement by cationic charge dispersion

Clay	Clay suspension electrolytic pH†	Indicator	$pK_a(1)$	$pK_a(2)$	% monocation	% dication
H-hectorite no. 34	2.7 ± 0.1	phenazine	1.2		92 ± 2‡	
H-hectorite no. 34	2.7 ± 0.1	*p*-nitroaniline	1.0		5 ± 2	
H-hectorite no. 34	2.7 ± 0.1	atrazine	1.7		15 ± 2	
H-hectorite no. 34	2.7 ± 0.1	5-aminoquinoline	5.4	1.0	25 ± 2	75 ± 2
Na-montmorillonite no. 25	6.5 ± 0.2	5-aminoquinoline	5.4		97 ± 5	
Na-montmorillonite no. 25	6.5 ± 0.2	3-aminopyridine	6.0		20 ± 5	
Na-montmorillonite no. 25	6.5 ± 0.2	2-amino-5-chloropyridine	4.8		5 ± 5	

* Clay suspensions (0.5 mg/ml) equilibrated 5 min with indicators 3.0 m-equiv. organic/100 g clay (dry weight basis).
† Electrolytic pH was measured in a stirred suspension 5 min after column saturation.
‡ Ranges represent multiple-sample spread.

enough organic molecules were tested to determine all the molecular structural factors involved in surface protonation. However, one observation seems noteworthy: protonation on surfaces is more highly dependent upon charge dispersion in the cationic indicator species than it is in solution (as measured by pK_a). Surface protonation is enhanced in systems containing multiple condensed ring systems as compared to single ring systems of similar solution pK_a. For example phenazine (three condensed rings) is protonated to a greater extent than is *p*-nitroaniline (one ring) or atrazine (one ring) in the same clay system (Table 2 and Fig. 2); also, 5-aminoquinoline (two condensed rings) is more highly protonated than the aminopyridines, (one ring), which have similar solution basicities.

Clay–water system variables

Clay preparation. To measure reproducibly the degree of protonation, the clay matrix must be homoionically saturated and relatively free of contamination from organic material and carbonate salts. The presence of carbonates markedly affects the degree of protonation (Bailey and Karickhoff, 1973). The clay minerals used were found to be sufficiently free of organic contaminants (<10 ppm), but some samples contained appreciable amounts of carbonates (>0.5%). Therefore, the decarbonation preparation stage was used routinely for all clays.

Clay type and source. Hectorite and montmorillonite were the only two clay types studied extensively; few kaolinites were investigated because their low adsorption capacity necessitates very low indicator concentrations relative to clay mass, the clay matrix has a high scattering background to the u.v. monitoring light, and their suspensions are unstable. Table 3 shows the effect of clay matrix and clay source on suspension protonation of 5-aminoquinoline. Figure 3 compares the protonation of phenazine on hectorite and montmorillonite films. For a given saturating cation and for a given indicator–clay ratio, hectorite and montmorillonites behaved quite similarly, whereas kaolinites (Table 3) showed a considerably lower degree of protonation. However, for equal indicator loading in terms of percentage of CEC, kaolinites showed considerably greater protonation than hectorites or montmorillonites. Figure 2 also shows

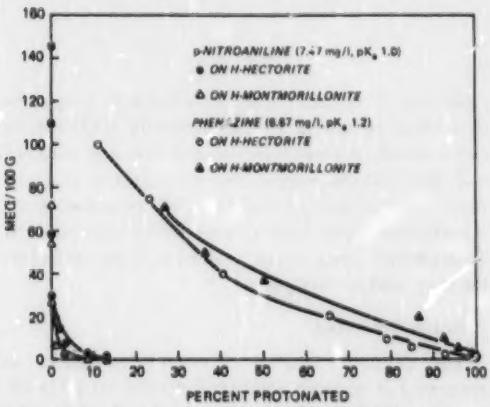

Fig. 2. Protonation of *p*-nitroaniline and phenazine on hectorite no. 34 and montmorillonite no. 25. Organic loading is expressed as m-equiv. organic indicator/100 g clay (dry weight). These units were chosen so as to be compatible with (and facilitate comparison with) the commonly quoted CEC values for adsorbent materials. Organo-clay suspensions were equilibrated five minutes after mixing.

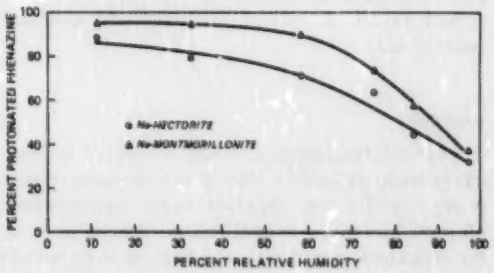

Fig. 3. Protonation of phenazine by hectorite no. 34 and montmorillonite no. 25 as a function of r.h.; 10.3 m-equiv. phenazine/100 g Na-hectorite; 10.7 m-equiv. phenazine/100 g Na-montmorillonite.

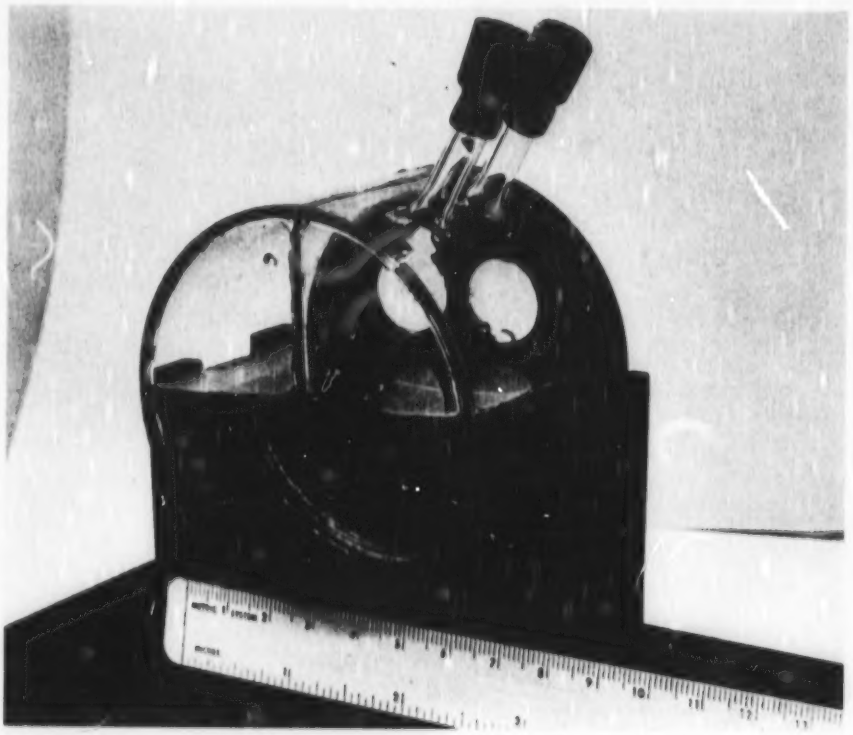

Fig. 1. Humidity control cell for clay films. The discs containing the sample films were recessed into the front face of the cell; the rear face is optical quartz.

Table 3. Clay suspension protonation of 5-aminoquinoline*

Clay mineral	Clay suspension electrolytic pH†	Clay concentration (mg/ml)	% protonation‡
Na–hectorite no. 34	6.2 ± 0.2	1.6	94 ± 2
Na–kaolinite no. 4	7.2 ± 0.2	1.5	30 ± 10
Na–montmorillonite no. 21	Not determined	1.5	91 ± 5
Na–montmorillonite no. 24	Not determined	1.4	93 ± 5
Na–montmorillonite no. 25	6.5 ± 0.2	1.5	97 ± 5
White Store	5.8 ± 0.2	1.1	51 ± 10
Iredell	6.7 ± 0.2	1.0	22 ± 10
Berks	5.6 ± 0.3	1.1	45 ± 10

* Clay suspensions were equilibrated 5 min with 5-aminoquinoline (15.0 mg/l).
† For the hectorite, kaolinite, and montmorillonites, electrolytic pH was measured in stirred suspensions 5 min after cations saturation via resin columns; the soil clay pH's were measured in stirred aged suspensions.
‡ Ranges represent multiple-sample spread.

the similarity in protonation behavior effected by hectorite and montmorillonite systems.

For the montmorillonite clays listed in Table 3, there appeared to be little or no dependence of protonation on clay source for the *freshly* prepared clay suspensions. Suspension properties such as stability and turbidity did vary with the different montmorillonites.

Saturating cation. The protonation of phenazine on montmorillonite varies with the type of saturating cation as shown in Fig. 4. When tested in turn with the three saturating cations, Ca^{2+}, Na^+, and H^+, montmorillonites, kaolinite and hectorite all showed the same relative cationic dependence of protonation ability in both suspension and film. All indicators were tested with all three cations on at least one type of clay, and all showed the same relative behavior with respect to saturating cation as did phenazine. For hectorite suspensions, in addition to Ca^{2+}, Na^+, and H^+, we tested Fe^{3+}, Mg^{2+}, and K^+. Protonation of indicators with a given saturation cation varied as follows:

$$H^+ > Fe^{3+} > Na^+ \sim K^+ > Mg^{2+} \sim Ca^{2+}.$$

Organic loading level. By holding the clay concentration in suspension (or the clay density in a film) constant and varying the amounts of organic material, the dependence of protonation on organic loading was shown to be significant. Figure 5 shows the organic loading effect on protonation in 5-aminoquinoline–Na hectorite suspensions. As the loading decreases from 75 m-equiv./100 g to 10 m-equiv./100 g, the percentage of neutral 5-aminoquinoline decreases from approximately 50 to approximately 2%. The dependence of protonation on loading rate also is shown in Fig. 2 in H^+–montmorillonite and H^+–hectorite suspensions; the degree of protonation of phenazine decreases from 95% protonated at 10 m-equiv./100 g to less than 25% protonated at a loading rate somewhat over 75 m-equiv./100 g.

Clay mineral concentration in suspension. When the organic loading was held constant, the degree of protonation did not vary significantly with the absolute clay concentration (as long as the clay levels were below the gel formation level), as illustrated in Fig. 5 for the 5-aminoquinoline–Na^+–hectorite system. In

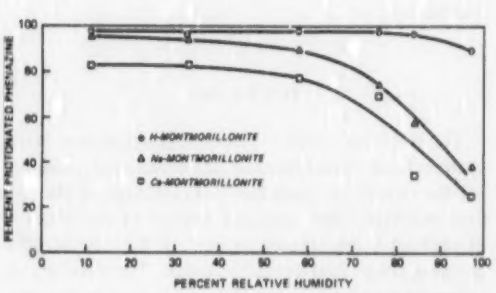

Fig. 4. Protonation of phenazine on montmorillonite no. 25 saturated with various cations as a function of r.h.: 10.7 m-equiv. phenazine/100 g clay.

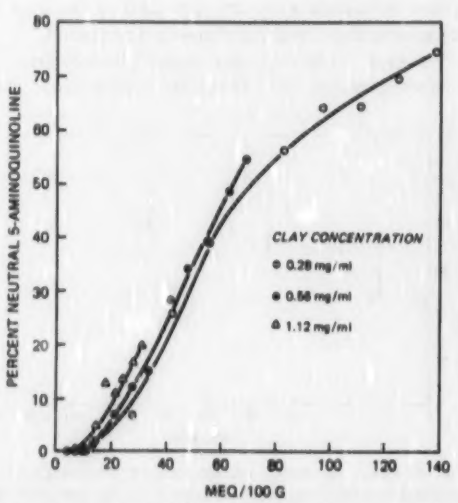

Fig. 5. Protonation of 5 aminoquinoline by Na–hectorite no. 34 as a function of organic loading rate. Equilibration time after organo-clay mixing was 5 min.

montmorillonites and hectorites, the degree of protonation decreased significantly at the onset of gelation. This reduction in protonation varied widely for different clay systems (i.e. with different saturating cations or lattices) and was not in general quantitatively reproducible. Upon drying beyond the gel state, clay–indicator systems showed a pronounced enhancement in protonation far in excess of that in a suspension.

Suspension aging. Much attention has been given to the chemical aging of clays (Paver and Marshall, 1934; Kerr *et al.*, 1955). It has been associated with the hydrolysis of saturating cations and/or edge sites. The ability of a given clay suspension to protonate the organic was maximal when freshly prepared. All measurements of suspension protonation described previously were performed within 10 mins of clay saturation and subsequent mixing with indicators.

As the suspension aged, the degree of protonation decreased, and the rate of decrease in protonation with time depended significantly upon saturating cation and clay type. The clays studied, in order of decreasing rate of change of protonation with time, were hectorites > montmorillonites > kaolinites; for a given clay structure the rate of change varied with cation in the order: $H^+ > Na^+ > Ca^{2+}$. In H^+–hectorite suspensions, an observable change in the extent of protonation takes place in a matter of minutes, whereas in Na^+–montmorillonite, a day or more is required to produce any appreciable decrease.

In some indicator–clay suspension systems, in addition to an irreversible decrease in indicator–protonation with time, a reversible change in protonation occurred when the indicator–clay suspensions were allowed to age undisturbed (without shaking or stirring beyond that required for initial mixing). This aging component could be reversed by shaking. The extent of the reversible aging and the speed of response to shaking were very dependent upon saturating cation, clay lattice, and clay concentration.

Figure 6 illustrates this aging phenomenon. A 5-aminoquinoline–Na^+–hectorite suspension was allowed to age in sealed cells and the % neutral indicator was measured as a function of time. The dark points in the figure designate the shaking of the sample and light circles indicate undisturbed monitoring. Shaking increased the degree of protonation of the 5-aminoquinoline each time, but never to the level measured in the initial (fresh) suspension, or even to the level attained at the previous shaking. During this period the *blank* hectorite suspension (i.e. containing no indicator) did not change significantly in optical density, indicating that the suspension had not settled out appreciably. As mentioned previously, protonation in a fresh suspension was not significantly dependent on clay concentration in this clay concentration range, so this reversible change in suspension acidity cannot be explained on the basis of the minimal settling that was observed. Passing the aged suspension through a Na^+-saturated cation exchange column restored the initial acidity.

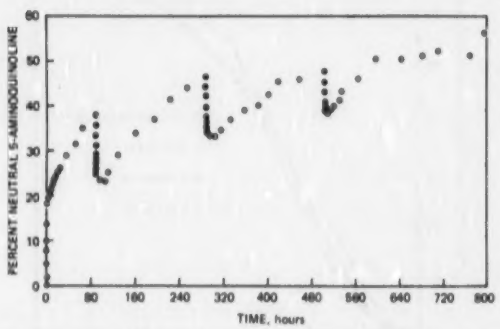

Fig. 6. Effect of aging on suspension protonation—5-aminoquinoline (5 mg/l) equilibrated with Na–hectorite no. 34 (2.5 mg/ml) was aged in sealed cells. ○ denotes undisturbed sample monitoring; ● designates shaking of the sample prior to monitoring.

Soil–clay systems

The protonation of 5-aminoquinoline by three soil clay suspensions is given in Table 3. The suspensions showed no change in the degree of protonation with time (over a two-day period). The degree of protonation appeared to be highly variable for multiple samples. This was in part due to the severe light, scattering problem associated with these clays and subsequent improper background-scattering compensation in the spectral analysis. Protonation in soil clay suspension was not in excess of that expected from electrolytic pH measurements.

Soil clay films posed several unique problems not found in the other clay systems studied. Upon drying, indicator–clay suspensions suffered a considerable loss of organic indicator—far in excess of that observed on other clay systems. The indicator that remained tended to "pool" in spots; the spectral indicator response varied as the clay–organic film was moved in the monitoring light beam. Indicator ressonse was not reproducible. With 5-aminoquinoline, the neutral, monoprotonated, and diprotonated species could often be found in the same spectrum. No effort was made to "clean" the soil clays (e.g. removing oxides, saturating the clay homoionically) so as to yield a more uniform-reproducible spectral response.

DISCUSSION

The use of an organic pesticide constitutes a deliberate release of a potential environmental pollutant for the benefit of mankind. A knowledge of the fate and potential environmental impact of pesticides is of particular importance in light of their rapidly increasing usage and extent of usage. The diversity in composition of pesticides, the multiplicity of formulations and modes of usage, and the complexity and heterogeneity of the soil systems afford tremendous

complexity to the description of the physical and chemical behavior of pesticides.

Of particular importance, although they are not well understood, are the many ways in which adsorption affects pesticide behavior. Adsorbed pesticide resides in an interfacial region between soil and aqueous phases. This interfacial region becomes important in the description of pesticide–water–adsorbent systems when (1) the interfacial volume becomes large compared to the total aqueous volume of the system, so that most of the available water is associated with adsorbent surfaces, (2) the pesticidal compound shows a high preference for the interfacial environment relative to bulk water (i.e. is highly adsorbed), or (3) the chemical behavior of the pesticide in the interfacial region is so drastically different as compared to its behavior in bulk aqueous systems that the phase-boundary processes govern the chemistry of the pesticide.

The nature of this interfacial environment depends not only upon the properties of solid and water phases involved, but most significantly upon the interaction between these two phases. For example dehydrated clay mineral surfaces function as Lewis acids (at sites of isomorphic metal substitution within the structure or edge sites) or Brönsted acids (hydroxylated surfaces) whereas hydrated clay mineral surfaces serve only as Brönsted acids (Helsen, 1970); the Lewis sites, when hydrated, are inactive to all Lewis bases weaker than hydroxide. One important source of surface protons is hydrolysis within the interfacial region of the saturating cations or structural sites. The behavioral properties of water or protons in this region are considerably different from those in bulk solution. Water contiguous to the surface has been reputed to be highly dissociated and of low dielectric constant (Touillaux *et al.*, 1968). Also the reactions of organic molecules with this water or protons differ considerably from those in bulk solvent. For example quinazoline, which typically forms a covalent hydrate (Albert, 1968) when protonated in solution, failed to hydrate when protonated in the interfacial region of a clay surface (Bailey *et al.*, 1973). Also, the covalent hydrate after having been formed in aqueous solution, slowly dehydrated upon addition of clay.

Protonation reactions of organic bases at a clay–water interface differ considerably from those in solution. Adsorption of the conjugate acid–base pair (equations 1 and 2) alters significantly the relative protonation tendencies compared to that reflected by solution pK_a.

Large condensed ring molecules are more highly protonated than smaller molecules of similar solution pK_a. The ability of a protonated base to disperse the positive charge over two or more rings tends to enhance protonation relative to solution behavior (Table 2, Fig. 2). Dications having positive charges in separate condensed rings protonated to a greater extent than dications with both charges in a single ring.

Many clay–water system variables significantly affect protonation equilibria. Just as the heat of adsorption of many organics on clays commonly decreases with increasing surface coverage, the ability of a surface to protonate additional base decreased with increasing surface coverage. This was observed in both the suspension and film states. For i.r. spectroscopic studies of organo-clay systems, the clay matrix must be saturated (or nearly saturated) with organic material because of the insensitivity of the monitoring technique. The chemical behavior of such a system could be significantly different from that of a system having an organic content of 10% of the absorbent CEC or less. To relate experimental results to typical adsorbent loading ranges for pesticides on sediment or soils in the field, it is important to study the behavior of the "low" end of the loading spectrum also. The u.v.-*vis* monitoring technique of following organic molecules is therefore valuable because it permits the monitoring of most clay adsorbents over a loading range from <1% of CEC to saturation.

Protonation equilibria in fresh suspensions (equations 1 and 2) were not particularly responsive to water content until the water content was reduced to the level at which most of the remaining water was associated with the phase boundaries. Protonation decreased significantly when the water content was reduced to the point of suspension gelation. This decreased protonation in clay gels relative to dilute suspensions is due to either an exclusion of the organic material from interlaminar adsorption sites in the gel structure or a reduction of available protons in the interlaminar gel structure relative to clay monomer surfaces.

The reversible reduction of protonation with aging (Fig. 6) of undisturbed organo-clay suspensions may be related to the formation of microflocs with a resultant reduction in protonation similar to that observed upon gelation. Shaking the aged suspension would then break up the clay aggregates, restoring the monomer acidity. The dependence of this aging phenomenon upon clay concentration is related to the probability of aggregate formation and/or dissociation, i.e. the suspension must be concentrated enough in clay monomers to facilitate aggregate formation upon standing, yet not so concentrated as to form a gel which cannot be broken up by shaking. The dependence of the phenomenon upon clay type and cationic saturation is related to the tendency of different clay systems to form aggregates and the stability of these aggregates once formed. For example Ca-hectorite seems to exist in an aggregated form that cannot be reversed by shaking, even in freshly prepared suspensions. This clay shows very little reversible aging. Also, this may explain the lack of indicator protonation in fresh Ca-clay systems relative to the monovalent counterparts.

In the clay films protonation increased monotonically as the film water content decreased throughout the moisture range studied (Figs. 3 and 4). The

enhanced protonation upon reduction of interfacial water is due to an "effective" increase in neutral indicator concentration in the interfacial water coupled with a destabilization of the hydrated proton. Both of these effects tend to displace the equilibria of equation (2) toward the protonated indicator. For equal indicator loading, the acidity of a clay film at 5% relative humidity (r.h.) was 4 or 5 "effective pH" units (relative to solution protonation) lower than that of the same clay in dilute suspension. For example at a loading of 1 m-equiv. of 5-aminoquinoline/100 g Na–hectorite, a dilute suspension showed nearly all monocation (Table 3), whereas in the film state at 5% r.h., 5-aminoquinoline existed almost entirely as the dication. The respective pK_a's of 5-aminoquinoline are 4.4 units apart in solution (Table 2).

The clay system variables, saturating cation and clay matrix, alter the acidity primarily by changing the protonic density on the surface. H^+–clays are more acidic than metal ion clays; trivalent metal-saturated clays are more acidic that their di- or monovalent counterparts. Noteworthy exceptions to this general rule are the divalent days, Mg^{2+} and Ca^{2+}, which have a lower acidity than the monovalent metal counterparts (Na^+ and K^+). A plausible explanation of this apparent anomaly was offered previously in terms of tactoid formation. The dependence of protonation on clay matrix types can be correlated with the density of saturating cations in a given clay; not enough clay types were investigated to determine all of the factors involved. Hectorite and montmorillonites behaved similarly. Kaolinites showed reduced acidity on a clay weight basis relative to hectorite and montmorillonite, but showed comparable or slightly increased relative acidity on a per-unit-CEC basis.

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